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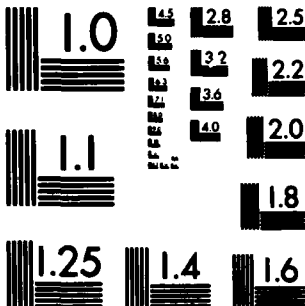
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OPTICAL AND ELECTRICAL PROPERTIES OF
YTTRIA STABILIZED ZIRCONIA (YSZ) CRYSTALS

by

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September, 1981

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20. Abstract

Optical transition spectra ($\lambda = 0.3-50 \mu\text{m}$) and dc conductivity (25°-1000°C) data were obtained on YSZ single crystals commercially grown by the skull melting process. The crystals were doped with up to 2.0 wt% rare earth (Ce, Nd, Er, Pr) and transition (Mn, Fe, Cr, Ni) metal ions, and a few were annealed. Dopant effects were most pronounced in the visible region, but were evident throughout much of the spectral range. Annealing and dopant ions Ce and Er showed significant absorption effects attributed to the Ce^{3+} ion. Electrical conductivity was only marginally affected by doping.

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Optical and Electrical Properties of
Yttria Stabilized Zirconia (YSZ) Crystals

by

R. C. Buchanan and S. Pope

Abstract

Optical transition spectra ($\lambda = 0.3\text{--}50\ \mu\text{m}$) and dc conductivity ($25^\circ\text{--}1000^\circ\text{C}$) data were obtained on YSZ single crystals commercially grown by the skull melting process. The crystals were doped with up to 2.0 wt% rare earth (Ce, Nd, Er, Pr) and transition (Mn, Fe, Cr, Ni) metal ions, and a few were annealed. Dopant effects were most pronounced in the visible region, but were evident throughout much of the spectral range. Annealing and dopant ions Ce and Er showed significant absorption effects attributed to the Ce^{3+} ion. Electrical conductivity was only marginally affected by doping.

I. Introduction

The system $\text{ZrO}_2\text{-Y}_2\text{O}_3$ (YSZ) has been much studied.^{1,2} This reflects the importance of ZrO_2 (stabilized) as a refractory material, for solid electrolyte and fuel cell applications and more recently as precise oxygen sensors for use in automotive and steel manufacture.

The effect of the Y_2O_3 additions is to stabilize the high temperature cubic ZrO_2 phase. Without adequate stabilization, the cubic fluorite phase transforms on cooling below $\sim 2300^\circ\text{C}$ to the tetragonal form, which in turn transforms to the stable low temperature monoclinic phase below $\sim 1150^\circ\text{C}$. This latter phase change is accompanied by a 4-5 vol% increase, which is disruptive of the structure.

It is now generally agreed that ~ 9 mol% Y_2O_3 addition is sufficient to fully stabilize the cubic ZrO_2 phase. In practice the $\text{ZrO}_2\text{-}9$ mol% Y_2O_3 composition has also been found to have the highest electrical conductivity in the system. As a result it is widely used for oxygen (gas) sensor applications, where high electrical conduction is a necessary design parameter.

Electrical conduction in the system $\text{ZrO}_2\text{-Y}_2\text{O}_3$ above 700°C is due almost entirely to high anion mobility ($t_{\text{O}^{2-}} > 0.99$) via vacancies.³⁻⁷ With 9 mol% Y_2O_3 , ~ 4.1 anion vacancies are created. The high electrical conduction observed for this relatively low anion vacancy concentration, therefore, reflects minimal defect interactions. Significant electronic conduction below 500°C has, however, been reported for YSZ doped with Fe^{3+} and other multivalent cations.⁸

Single crystals of YSZ have recently been prepared by the skull-melting process.^{9,10} This technique allows the growth of relatively large crystals of refractory dielectric materials (YSZ crystals > 15 cm dia. have been

grown). A water-cooled crucible or 'skull' is used to contain the molten dielectric within a crust or jacket (~ 1 mm thick) of its own composition. The skull is shaped such that radio frequency energy can pass through into the batch to heat and melt the powder charge. In the case of YSZ, initial heating of the dielectric powder is provided by Zr metal susceptors placed in the middle of the batch. At temperatures above $\sim 900^\circ\text{C}$, where the YSZ powder becomes sufficiently conducting, the metal is no longer needed and oxidizes to augment the batch composition. Columnar crystals, often twinned, are obtained from the melt by directional solidification during cooling. Different colored crystals may be produced in this process, by incorporating low concentrations (< 2.0 wt%) of multivalent or rare earth oxides into the batch.

Detailed studies by Aleksandrov^{11,12} on optical homogeneity of the skull-grown YSZ crystals showed the most characteristic defect to be cords running perpendicular to the crystal growth axis $[011]$. Small concentrations of such oxides as CeO_2 , Er_2O_3 and Nd_2O_3 were found to generate particulate defects in the range $0.03\text{ }\mu\text{m}$ – $8.0\text{ }\mu\text{m}$, which acted as scattering sites. Annealing of the crystals above 1200°C in an oxidizing atmosphere, reduced the stresses as well as the defect level and dislocation density, making the crystals essentially isotropic. The refractive index (n) measured for the 9 mol% Y_2O_3 crystals was in the range 2.11–2.17, with coefficient of dispersion, $v \sim 31.50$. These values decreased for higher Y_2O_3 content, and varied to a lesser extent with heat treatment and the amount of added rare earth or transition element. Optical absorption spectra for a number of these elements at oxide concentrations of ~ 0.5 wt% were also recorded between $0.22\text{ }\mu\text{m}$ – $1.0\text{ }\mu\text{m}$. Characteristic absorption peaks were obtained which could be modified by irradiation or annealing treatment.

As indicated, the YSZ crystals possess a high refractive index and dispersion, close to that of diamond ($n = 2.42$, $\nu = 27$). The crystals are also transparent throughout the visible and near infrared spectral ranges ($\lambda = 0.35 - 7.0 \mu\text{m}$). With a hardness factor in the range 7.5-8.5 Mohs, depending on Y_2O_3 content, this combination of properties makes good quality YSZ crystals an attractive synthetic substitute for gem quality diamonds—for which purpose they are mainly used. Other uses include lenses, prisms, laser applications, and infrared sensors or windows, this latter because of the high spectral transmission in the range $\lambda = 3 \mu\text{m} - 7 \mu\text{m}$. YSZ crystals have also been considered for oxygen sensor and for fuel cell applications.

Little data exists, however, on the electrical properties of the YSZ crystals, particularly when doped with rare earth and multivalent cations. Likewise the effect of this doping on the infrared transmission spectra has not been determined. The object of this study, therefore, was to characterize the effects of the various dopants on the optical and electrical properties of YSZ crystals.

Samples used in this study were 9.5 mol% Y_2O_3 (YSZ) crystals prepared by Ceres Corporation [Waltham, Mass.] using the aforementioned skull-melting process. Rare earth and transition element dopants up to 2 wt% oxide were incorporated into the crystals. A few samples were also annealed. A 12 mol% Y_2O_3 crystals was used for comparison. Optical transmission spectra were developed for the range $\lambda = 0.3 \mu\text{m} - 50 \mu\text{m}$ for each of the samples. Electrical resistivity (dc) measurements were made up to 1000°C .

II. Experimental Procedures

1. Composition

As indicated, single-crystal YSZ samples used in this study were prepared by the skull-melting process and were supplied by the Ceres Corporation [Waltham, Mass.]. Composition for the various samples are given in Table 1. The base compositions for the crystals was ZrO_2 -9.5 mol% Y_2O_3 , to which small concentrations of dopant or coloring oxides were added, as detailed in Table 1. The dopant cations have all been shown to cause the development of color in the cubic ZrO_2 - Y_2O_3 single crystal lattice,⁹ and the different combinations were designed to develop particular colors. Several samples contained CeO_2 (typically 0.1 wt% but also at 1.0 wt% and 2.0 wt%) alone or in combination with other dopants. The CeO_2 aided in the control of the various colors. Most samples were supplied in the unannealed state, whereby some cerium ions would be in the reduced (Ce^{3+}) state.¹¹ Two samples (No.'s 1 and 8, Table 1) were received in the annealed state. This had been carried out in air at 1200°C/24 h, and was intended to re-oxidize any reduced ions as well as reduce the overall defect levels in the crystal. This allowed direct comparison with samples 1, 2 and 7, 8, which were of identical composition.

2. Optical Spectra

Samples for optical evaluation were prepared from each crystal. The samples were cut plane parallel about 2 mm thick in a direction normal to the growth axis. Nominal diameters were about 2.0 cm. The samples were polished on both sides to transparency using 600 SiC [Carborundum] grit and 15 μm and 6 μm diamond paste. Care was taken to avoid too reflective a surface on the specimen faces.

Table 1
Composition of YSZ (9.5 mol% Y_2O_3)
Single Crystal Samples
Dopant/Concentration (Wt%)

Sample	Color	CeO ₂	MoO ₂	FeO	CeO	NiO	Pr ₂ O ₃	Nd ₂ O ₃	Er ₂ O ₃	Cr ₂ O ₃
1*	Clear	0.1	—	—	—	—	—	—	—	—
2	Organge	0.1	—	—	—	—	—	—	—	—
3	Red-Org.	2.0	—	—	—	—	—	—	—	—
4	Straw	—	0.1	—	—	—	—	—	—	—
5	Lt. Yel.	—	0.05	—	—	—	—	—	—	0.5
6	Yellow	—	—	0.1	—	—	—	—	—	—
7	Dark Violet	—	—	—	0.2	—	—	—	—	—
8*	Violet	—	—	—	0.2	—	—	—	—	—
9	Dk. Red	1.0	—	—	0.3	—	—	—	—	—
10	Amber	0.1	—	—	—	0.1	—	—	—	—
11	Salmon	—	—	—	—	0.1	—	—	1.0	—
12	Pink	0.1	—	—	—	—	—	—	1.0	—
13	Gold. Yel.	—	—	—	—	—	0.2	—	—	—
14	Clear	0.1	—	—	—	—	—	0.22	—	—
15	Lt. Gray	0.1	—	—	—	—	—	0.44	—	—
16**	Clear	—	—	—	—	—	—	—	—	—

*Air annealed—1200°C/24 h.

**YSZ (12 mol% Y_2O_3).

Each sample was optically scanned over the spectral range 0.3 μm to 50 μm , incorporating both the visible and infrared ranges. For the IR ranges (50 μm -2.5 μm) a Beckman IR-12 Spectrophotometer was used in the double-beam mode. A Nicolet FT-IR Spectrophotometer was also used over the same IR range and permitted more accurate interpretation of the data. Wavelengths spanning the near infrared and visible regions (2.5 μm -0.65 μm) and (0.65 μm -0.3 μm) were scanned using a Cary-14 Spectrophotometer.

3. Electrical Conductivity

Samples for electrical conductivity measurements were cut plane parallel as described previously and shaped geometrically to approximately 1 cm x 1 cm x 0.2 cm. Electrodes were applied to both faces of the sample using platinum paste which was fired at 800°C for 10 min. Measurements were carried out as a function of temperature to ~ 1000°C using a Keithley 610-B electrometer. The specimens were heated in a vertical, shielded platinum-wound tube furnace up to 1000°C at a heating rate of ~ 10°C/min. A flat platinum stage (supported on Al_2O_3) served as contact base and a spring-loaded platinum tipped probe as the upper electrode. The temperature sensing thermocouple was positioned next to this probe.

III. Results and Discussion

1. Visible Spectra

Table 1 shows the wide spectrum of coloration imparted to the basic YSZ crystals by the various dopants. Grouping of these dopants could be made according to the colors produced in the crystals which, in general, were similar to the colors produced in glasses. Yellow hues, for examples, were predominantly produced by Mo, Cr, Re, and Pr dopants, generally in the absence of Ce. These ions would likely be present in the 3^+ state.

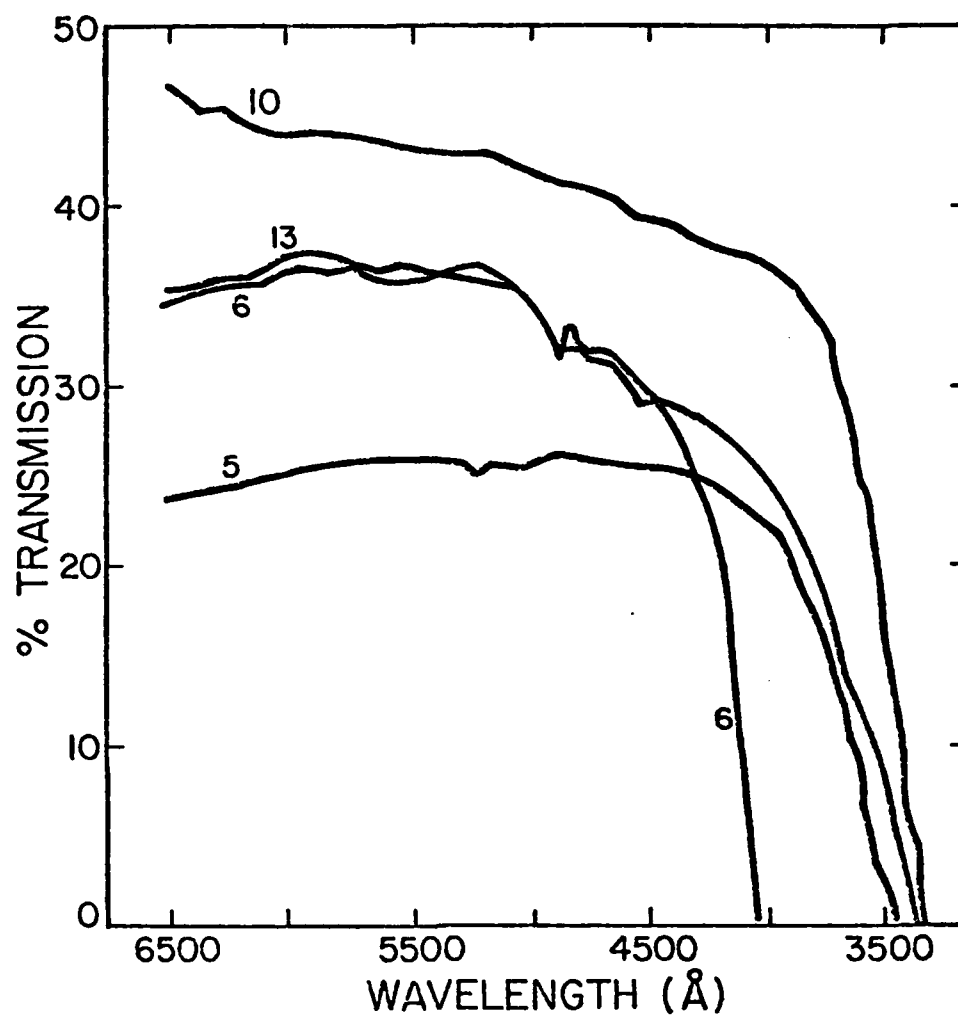


Fig. 1. Optical transmission spectra for YSZ crystals with dopants 5(Mo/Cr), 6(Fe), 10(Ce/Ni), and 13(Pr) as given in Table 1.

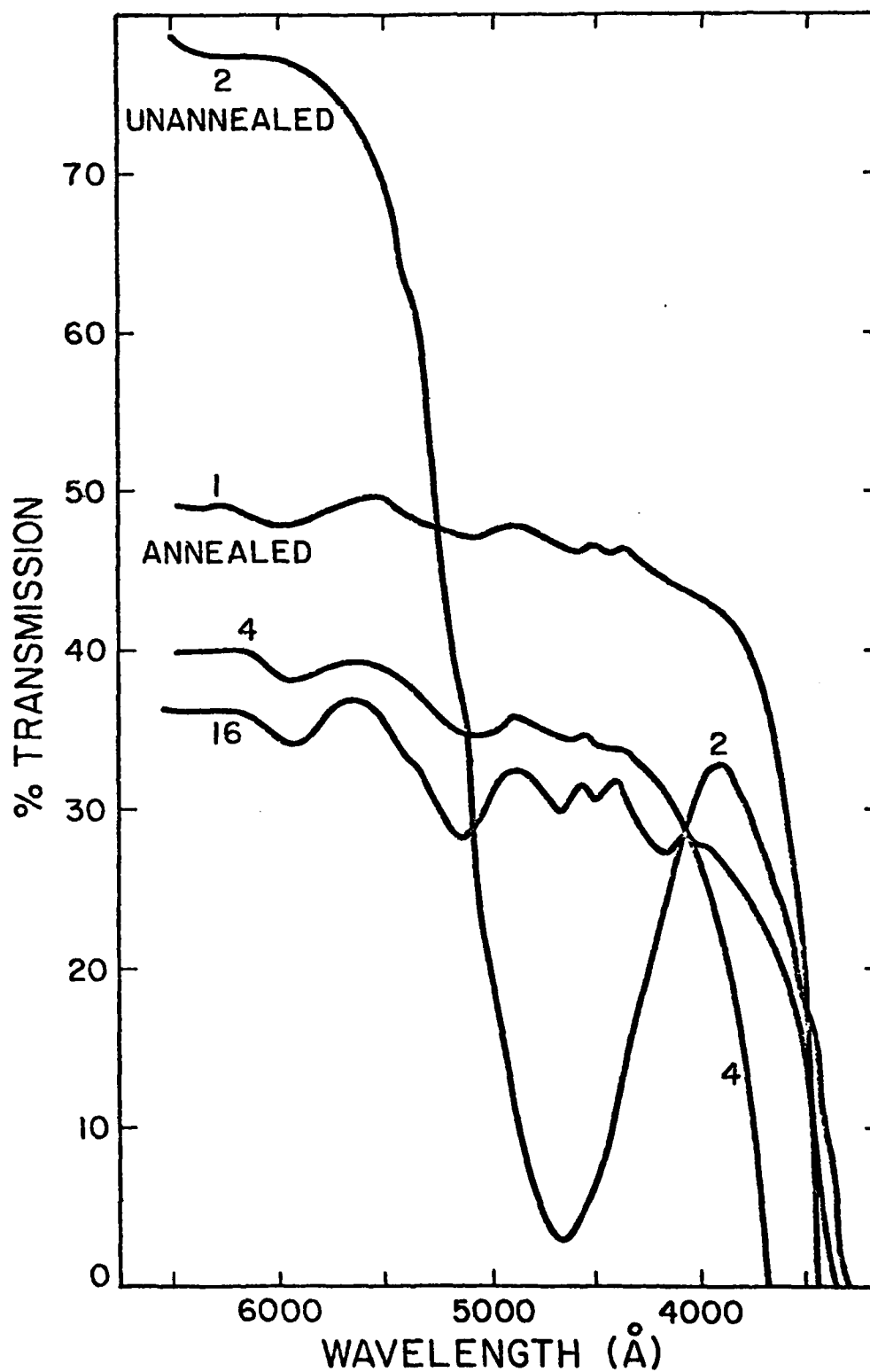


Fig. 2. Optical transmission spectra for YSZ crystals with dopants 1(Ce), 2(Ce), 4(Mo), and 16(none) as given in Table 1.

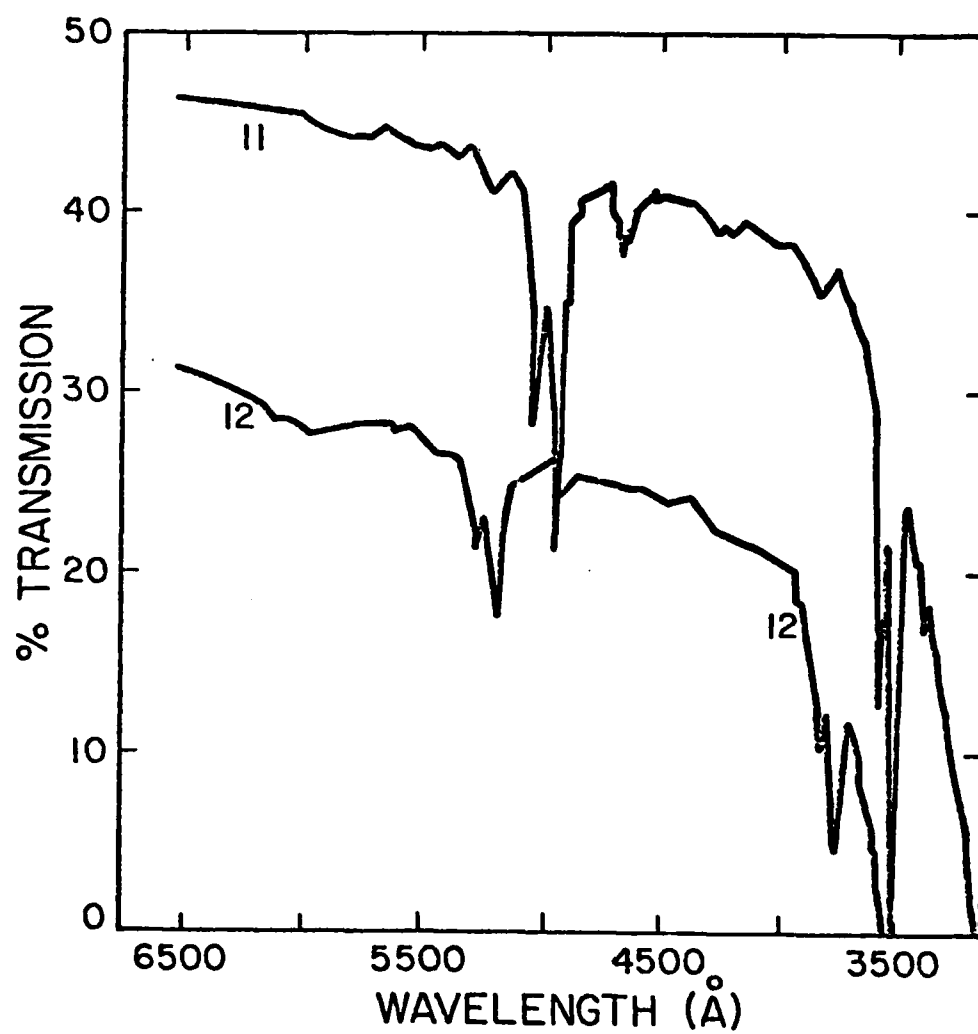


Fig. 3. Optical transmission spectra for YSZ crystals with dopants 11(Ni/Er) and 12(Ce/Er) as given in Table 1.

Transmission spectra in the visible range are given for these dopants in Fig. 1. Numbering of the curves in the figures correspond to the data in Table 1.

Relative transmission values may not be strictly comparable, however, due to differences in sample thickness and surface finish. The spectra show generally good transmission in the range 4500 \AA – 6500 \AA , with the absorption edge around 3400 \AA ($\sim 1.4 \text{ eV}$), except for Fe doping (Curve 6) which showed a significant shift of the absorption edge to $\sim 4100 \text{ \AA}$. This is in line with the well-known absorption of the blue (ultraviolet) end of the spectrum by Fe^{3+} ions in glasses. Other than the shift of absorption edge, no significant absorption peaks were observed in this spectral region.

The basic YSZ crystals were clear or colorless (sample 16 in Table 1) and moderately transmitting in the visible region, as shown in Fig. 2. Addition of Nd also gave clear crystals which became progressively more grey with increase in Nd content (samples 14 and 15).

Doping with Ce imparted an orange coloration to the crystal (sample 2) tending to red (sample 3) as the Ce concentration was increased. Annealing of the Ce doped crystals removed the coloration and gave a normal spectra (sample 1, Fig. 2). The spectra for the unannealed sample shows high transmission in the red region and significant absorption at $\sim 4700 \text{ \AA}$, attributed to a significant concentration of Ce^{3+} ions. The similarity of the spectra for samples 1, 16, and 4 (Mo/Cr) would suggest that the ions substitute on regular cation sites in YSZ lattice.

Apart from Ce^{3+} , the only strong absorption peaks observed were for Er doping (samples 11 and 12). Figure 3 shows these spectra where strong absorption peaks were obtained in the ranges 5200 \AA – 4900 \AA and 3800 \AA to 3500 \AA . Again this was attributed to absorption by the Er^{3+} ions.

A strong deep blue color was obtained with Co doping which became lighter after annealing (samples 7 and 8), reflecting the decrease impurity level. Combination of Ce with Co produced a dark ruby red crystal (sample 9).

2. Infrared Spectra

Figures 4, 5, and 6 show IR spectra for the different crystals in near (0.65-2.5 μm), medium (2.5-10 μm) and far (7.0-50 μm) infrared regions, respectively. Figure 4 shows transmission in the near infrared range to be relatively high, with little absorption activity except for crystals 1, 11, 16, and 12.

Considering the sample compositions, the absorption peaks in the region of 1.5 μm seem clearly associated with the presence of Ce and Er since both are missing in the undoped sample 16. Peaks at ~ 1.2 and 2.2 μm would seem to be associated with the presence of Y^{3+} in the ZrO_2 lattice.¹¹ This area of the spectrum has not been well studied.

Figure 5 shows the infrared transmission up to 10 μm for the crystals studied. All showed an IR cutoff at ~ 7 μm . Highest transmitting crystals were numbers 2 and 1 (low Ce) and lowest numbers 10 (Ce/Ni) and 5 (Mo/Cr), attributed to the presence of the transition metal ions. In general, any dopant addition to the YSZ crystals tended to decrease the IR transmission in this range. Significant absorption peaks were observed only for samples 3 and 9, reflecting the relatively high Ce content in these crystals.^{2,11}

Figure 6 shows a generalized curve for the crystals in the IR range 7-50 μm , since the transmission characteristics were essentially identical for all samples. The crystals were essentially opaque up to ~ 17 μm and showed significant transmission at the longer wavelengths.² The fine

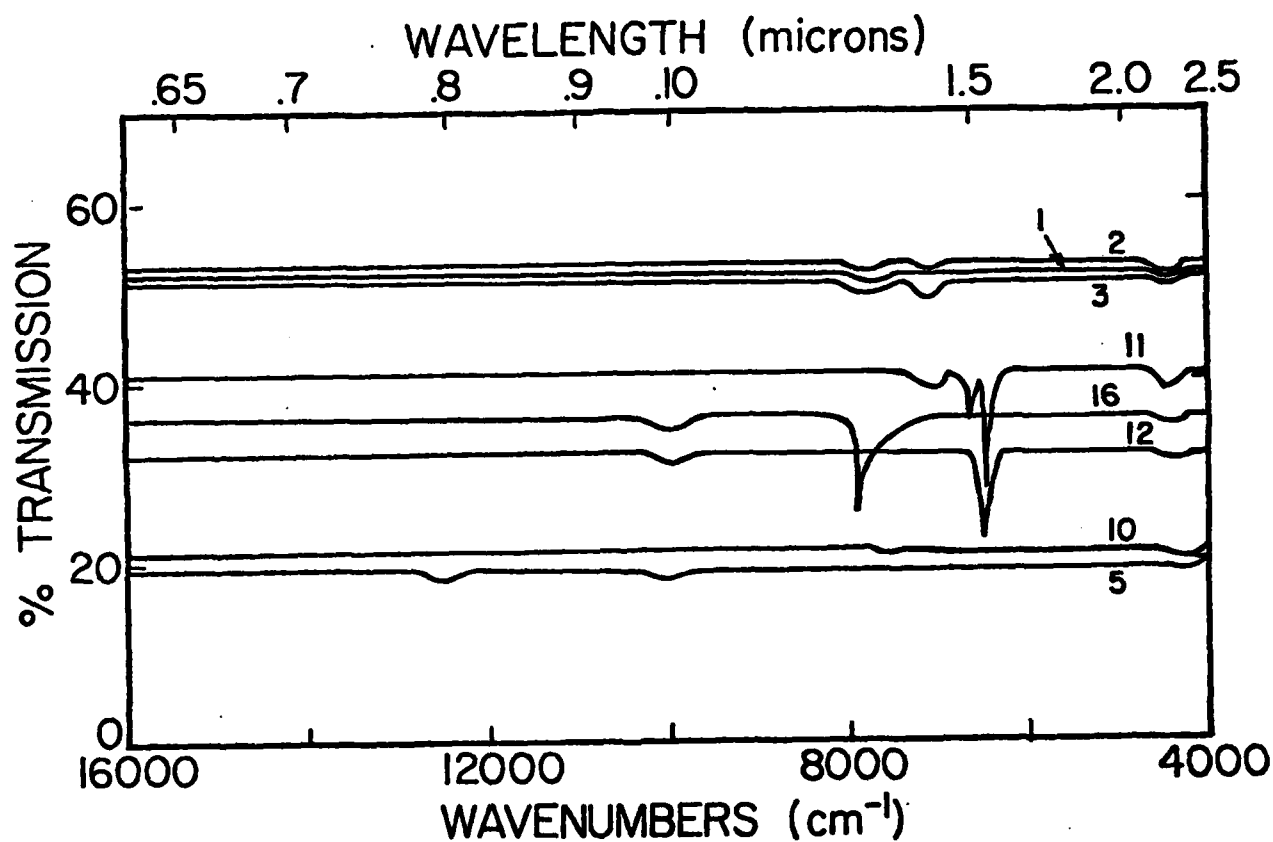


Fig. 4. Near infrared transmission spectra for YSZ Crystals Nos. 1, 2, 3, 5, 10, 11, 12, and 16 in Table 1.

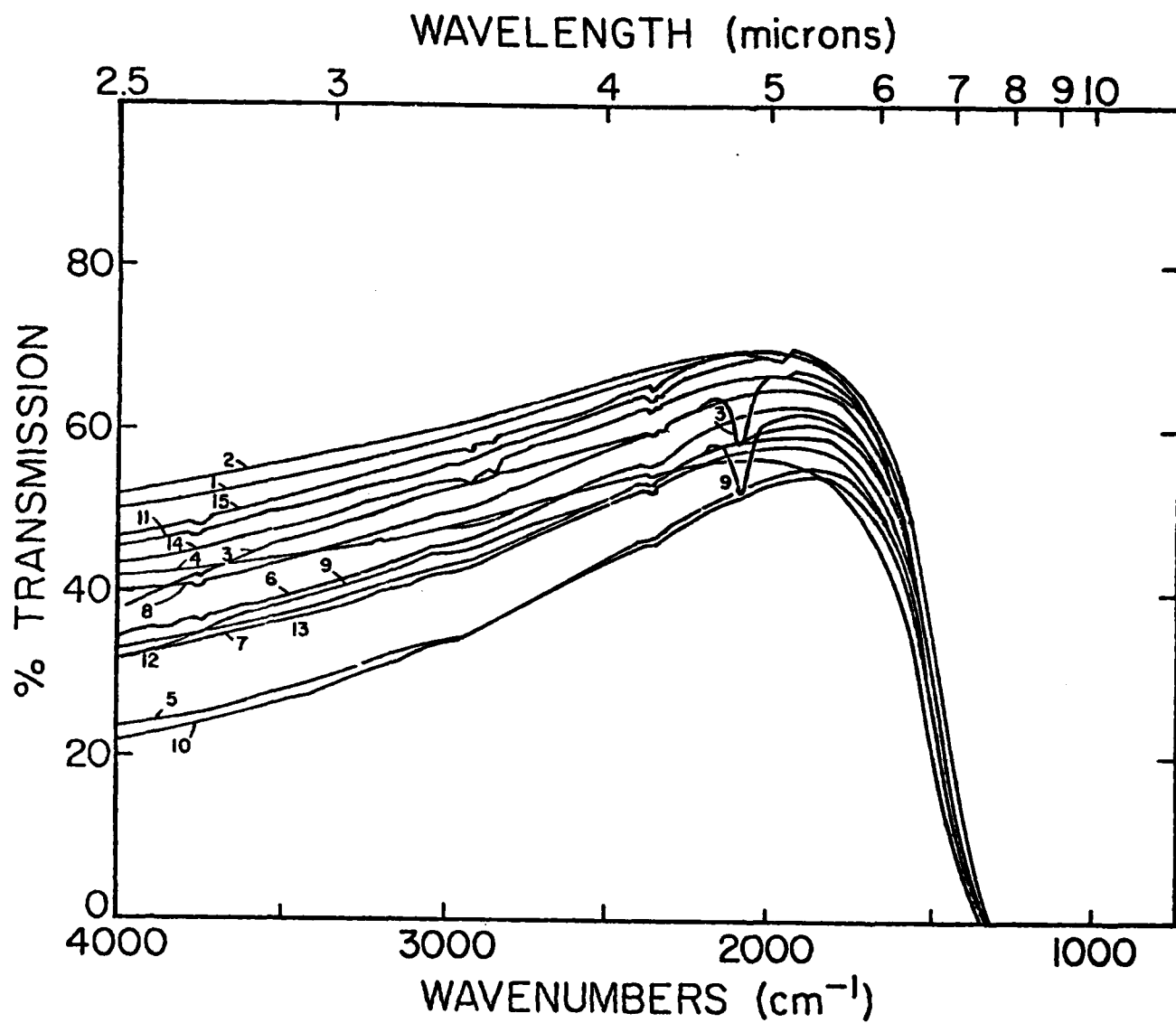


Fig. 5. Medium infrared transmission spectra for the YSZ crystals in Table 1.

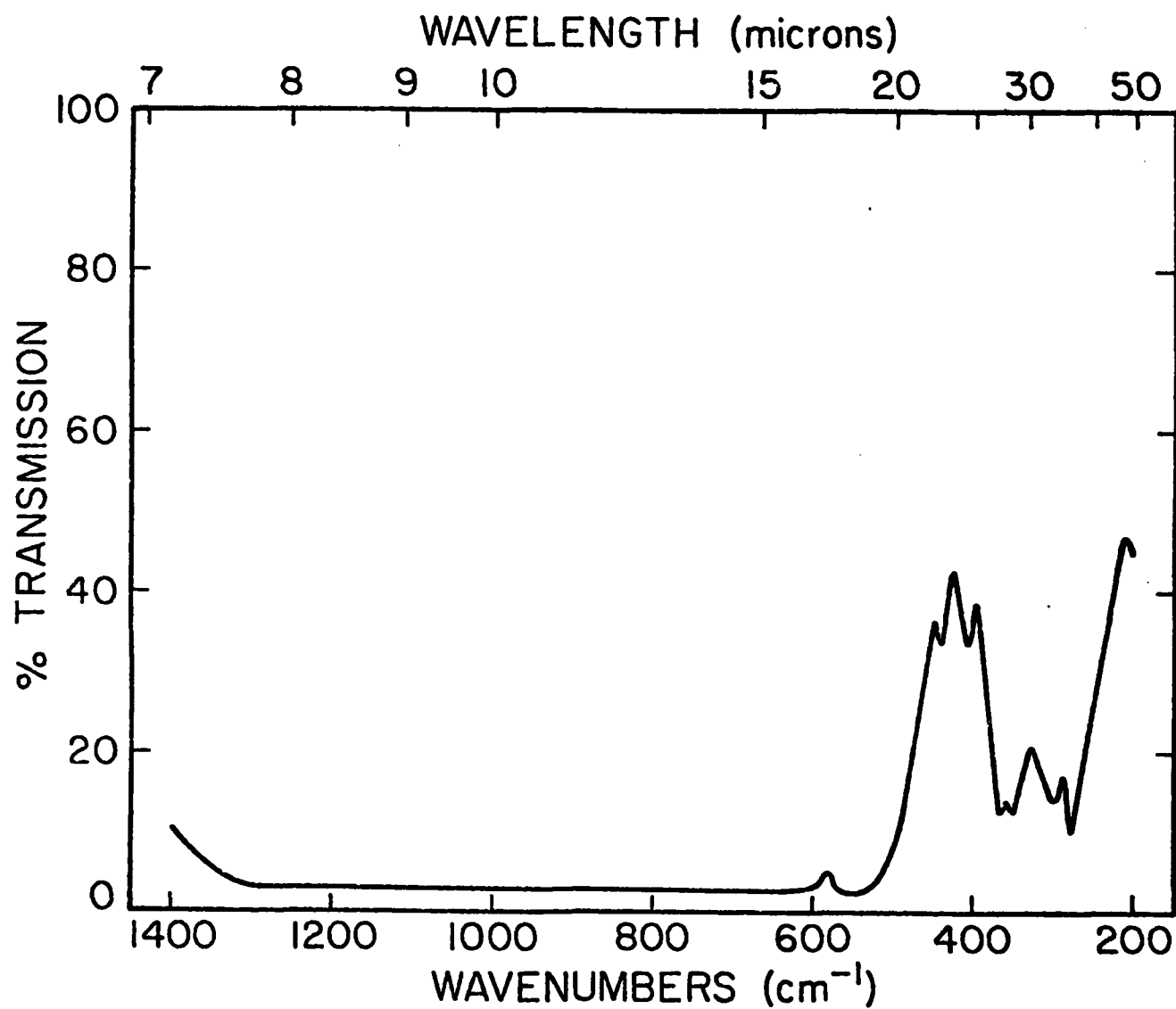


Fig. 6. Typical far infrared transmission spectra for the YSZ-(9.5 mol% Y_2O_3) single crystals.

Table 2
Electrical Conductivity for YSZ Crystals with Temperature

Sample	Dopants	Conductivity- $(\Omega\text{-cm})^{-1}$				E_A (eV)
		200°C	500°C	800°C	1000°C	
1*	CeO ₂	4.71×10^{-8}	7.37×10^{-4}	7.06×10^{-2}	1.28×10^{-2}	1.02
2	CeO ₂	2.89×10^{-8}	3.77×10^{-4}	2.42×10^{-2}	3.99×10^{-2}	0.99
3	CeO ₂	2.82×10^{-8}	5.25×10^{-4}	2.47×10^{-2}	3.56×10^{-2}	1.01
4	MoO ₂	6.17×10^{-9}	3.36×10^{-4}	2.89×10^{-2}	4.95×10^{-2}	1.05
5	MoO ₂ /Cr ₂ O ₃	1.59×10^{-8}	2.31×10^{-4}	1.42×10^{-2}	2.06×10^{-2}	1.00
6	FeO	4.89×10^{-8}	7.13×10^{-4}	1.94×10^{-2}	3.89×10^{-2}	0.97
7	CoO	2.74×10^{-8}	5.37×10^{-4}	2.84×10^{-2}	4.35×10^{-2}	1.02
8*	CoO	3.64×10^{-8}	2.26×10^{-4}	2.48×10^{-2}	3.64×10^{-2}	1.00
9	CeO ₂ /CoO	2.30×10^{-8}	1.67×10^{-4}	2.38×10^{-2}	4.63×10^{-2}	1.02
10	CeO ₂ /NiO	1.13×10^{-8}	2.23×10^{-4}	1.67×10^{-2}	2.5×10^{-2}	1.03
11	NiO/Er ₂ O ₃	2.65×10^{-8}	3.63×10^{-4}	1.63×10^{-2}	2.49×10^{-2}	1.01
12	CeO ₂ /Er ₂ O ₃	1.60×10^{-8}	4.21×10^{-4}	2.63×10^{-2}	3.86×10^{-2}	1.05
13	Pr ₂ O ₃	1.19×10^{-8}	2.00×10^{-4}	2.35×10^{-2}	3.7×10^{-2}	1.05
14	CeO ₂ /Nd ₂ O ₃	1.77×10^{-8}	2.76×10^{-4}	1.92×10^{-2}	3.22×10^{-2}	0.99
15	CeO ₂ /Nd ₂ O ₃	2.02×10^{-8}	2.03×10^{-4}	1.60×10^{-2}	2.18×10^{-2}	0.99
16	None	4.32×10^{-9}	4.32×10^{-4}	1.75×10^{-2}	2.32×10^{-2}	1.16

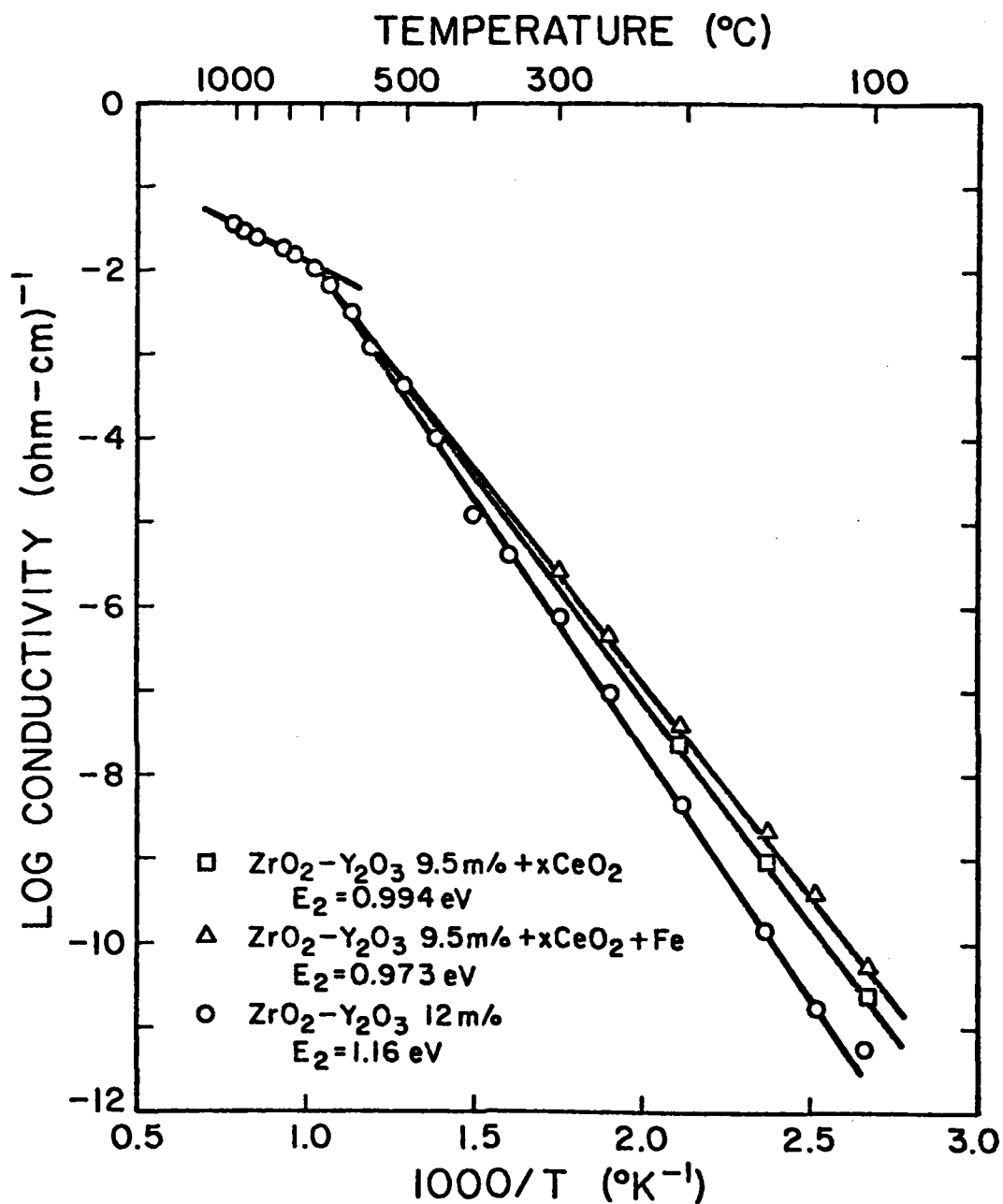


Fig. 7. Log conductivity versus reciprocal temperature for YSZ (12.0 mol% Y₂O₃) and YSZ (9.5 mol%) crystals with different dopants. Activation energies, E₂, was calculated from data below 800°C.

structure of the spectra represents bonding characteristics within the fluorite structure.

3. Electrical Conductivity

Table 2 gives electrical conductivity data at 200°, 500°, 800°, and 1000°C for the different YSZ samples with dopants including activation energy values. For the 9.5 mol% YSZ samples, dopant level or type dopant was found to have little direct effect on conductivity of the crystals. The annealed Ce (sample 1) and those with transition metal (Fe, Mo, Cr, Ni) dopants gave slightly lower conductivities, but activation energy values were comparable. The 12 mol% YSZ samples gave a lower value for the conductivity and correspondingly higher activation energy, as expected.

Figure 6 shows a plot of log conductivity versus reciprocal temperature for the 9.5 YSZ sample with dopants and the undoped 12 mol% YSZ sample. Only the latter showed any significant difference in activation energy, indicated by the steeper slope below ~ 800°C. The change of slope in the conductivity curve above 800°C had not previously been reported for YSZ. Below 800°C, both conductivity and activation energy values were comparable.^{1,2,6}

IV. Conclusions

1. For YSZ samples containing 9.5 mol% Y_2O_3 , dopant and annealing effects were particularly noticeable in the visible spectra. Ce, Er, Fe, and Co doping showed the most significant changes. Effect of annealing was apparently to reduce Ce^{3+} and defect concentration.
2. The IR spectra appeared less affected by dopants, except in the near infrared. Relatively high transmission was obtained for all crystals up to ~ 7 μm cutoff.
3. Dopant influence on electrical conductivity was not significant.

Changes in the Y_2O_3 content had a greater effect. Measured activation energy for conduction of ~ 1.0 eV and conductivity of $\sim 2 \times 10^{-2} \text{ (ohm-cm)}^{-1}$ at 800°C , were typical of the YSZ samples.

V. Acknowledgements

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Summary of Work Accomplished
Under Contract No. US NAVY-N-00014-80-K-0969

1. Reports

Report issued under this contract include the following:

- a. R. C. Buchanan and S. Pope, "Optical and Electrical Properties of Yttria Stabilized Zirconia (YSZ) Crystals," (ONR Report #5), University of Illinois, Urbana, IL (September 1981).
- b. R. C. Buchanan and J. Boy, "Effect of Coprecipitation Parameters on Powder Characteristics and On Densification of PZT Ceramics," (ONR Report #6), University of Illinois, Urbana, IL (September 1982).
- c. R. C. Buchanan and D. Wilson, "Development of Optically Translucent Yttria Stabilized Zirconia (YSZ) Ceramics Below 1300°C with Alumina and Borate Additives," (ONR Report #7), University of Illinois, Urbana, IL (November 1982).

3. Papers

- a. R. C. Buchanan and S. Pope, "Optical and Electrical Properties of Yttria Stabilized Zirconia (YSZ) Crystals," Accepted, J. of Am. Ceram. Soc., 1982.
- b. R. C. Buchanan and J. Boy, "Effect of Coprecipitation Parameters on Powder Characteristics and On Densification of PZT Ceramics," submitted to J. of Am. Ceram. Soc., 1982.